be discussed based on a general treatment of processes 1-3 above. In addition, the modifications of diffusion processes on extracted *P-T* can be shown to be non-trivial.

Note that nowhere is time included in *P-T* paths except with additional geochronology. Interestingly, the expected modifications by (2) and (3), however, lead to a potentially much more powerful inversion that can extract *P-T*-t paths. The power of such an inversion has only very recently been appreciated and applications of zoning profiles to constraining possible tectonic processes are just now being carried out. Applications of the inversion approach to cation exchange in garnets, cation exchange in sphalerite, and oxygen isotopic exchange in silicates will be discussed. Field applications will include contact metamorphism in the Cortlandt Complex, New York and regional metamorphism in the Chiwaukum Schist of the Cascade Mountains of Washington State.

Stable isotopic disequilibrium in high-*T* metamorphic systems

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A principal use of stable isotopes in metamorphic rocks is as thermometers, or as tests for isotopic equilibrium where metamorphic temperatures are known. Applications are often complicated when apparent isotopic temperatures are discordant and disagree with petrologic temperatures, indicating a failure of isotopic systems to record and/or preserve equilibrium, peak-*T* fractionations. In low-*T*, fluid-hosted environments such features often clearly reflect open system exchange. However, in high-*T* metamorphic environments a slow cooling history can be sufficient to produce such features by retrograde, *closed system* exchange between coexisting minerals.

Ample evidence for retrogression can be found in amphibolite and granulite facies rocks. The correspondence between experimentally determined diffusion coefficient and field evidence of retrogression for several minerals suggests the importance of interdiffusion during cooling. Specific examples include: discordance and resetting in rocks containing minerals of the quartz-feldspar-muscovite-biotite, magnetite-carbonate and magnetite-silicate systems (all minerals with moderate to high *D*), and relatively concordant and non-reset thermometers involving garnet, pyroxene and olivine (minerals with low *D*). Much of our understanding of diffusion-controlled retrogression has been based on Dodson's 'closure temperature'. But a number of questions must be answered before our understanding of the relationship between diffusion and disequilibrium in high-*T* rocks can reach a predictive and quantitative level. In the absence of any direct observation that minerals are isotopically zoned in a way consistent with diffusional exchange, inferring diffusion-control from failed thermometry alone is problematic. Furthermore, even if diffusional re-equilibration is responsible for the disequilibrium seen, analytical expressions derived for diffusional loss in geochronologic systems cannot be applied to isotope exchange of major elements.

Recent advances in analytical technique and mathematical models have allowed researchers to address some basic questions about isotope diffusion in metamorphic environments. Numerical modelling reveals the strong control that modal composition can have on the mass-balance of diffusional exchange and apparent isotopic temperatures. Ion microprobe studies of oxygen isotope zonation in magnetites from the slowly cooled granulites of the Adirondack Mts, N.Y., USA have provided the first direct evidence for diffusional zonation in minerals, but have also revealed complex intercrystalline zonation involving fluid-hosted alteration. Differences in the results of thermometry between these two cases can be subtle, making any one fractionation difficult if not impossible to interpret. However, ion microprobe evidence for diffusion controlled retrogression has been found in all samples studied to date in which diffusion modelling, and thermometry predict its presence. Diffusion-controlled retrogression seems then to be common but not ubiquitous, and can be reasonably inferred only with detailed thermometric and petrologic data.

The rate of diffusion along grain boundaries is as important as intracrystalline diffusion rates in determining the effects of retrograde exchange in high-*T* environments. Where diffusional exchange during retrogression is enhanced by grain boundaries, cm-scale exchange between lithologoic layers and partial re-equilibration between non-touching grains can take place. These effects have direct ramifications on the mathematical models we use to relate experimental diffusion coefficients to the isotopic disequilibrium we see in rocks.

Existing calibrations of grain boundary diffusion rates have yielded contradictory results, and have been measured under conditions that are substantially different from those in the deep crust. A study employing laser-probe and ion microprobe analysis of stable isotope zonation across a lithologic contact in Adirondack

granulites has determined the rate of grain boundary diffusion in a regional metamorphic setting. Results support the importance of very rapid grain boundary transport in granulite facies environments, which are typified by low water activity and coarse, annealed textures. An additional case study of textural control on isotopic composition in granulite facies rocks reveals how volume diffusion and grain boundary diffusion combine to produce complex inter- and intra-crystalline zonation on the thin-section scale.

Kinetics of fluid-mineral reactions in prograde metamorphic processes

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The rates of metamorphic reactions that produce prograde mineral assemblages observed in a rock can be considered in the context of possible rate limiting mechanisms. As the temperature increases towards the peak metamorphic temperature, the Gibbs energy of the higher grade assemblage minus the Gibbs energy of the lower grade assemblage becomes negative. With this Gibbs energy drive the reaction proceeds by a number of sequential steps with the slowest being rate limiting. These are: the dissolution of the reactant mineral in the grain boundary fluid along the reactant mineral surface; migration of reactant material in this fluid by diffusion and/or advection to a site of heterogeneous nucleation; and then nucleation and growth of the product mineral.

The rates of transport of material through solid state or grain boundary diffusion are too slow for the chemical potential gradients involved to cause significant reaction even in the tens of millions of years of regional metamorphic events for the distances of a couple of mm that the material needs to be transported. This implies that a fluid must be present to cause significant reaction. Depending on the flux of fluid, the reaction rate can be either mineral surface controlled or controlled by transport in the fluid phase. In large part this is dependent on the way fluid produced by devolatation reactions during prograde metamorphism is channelized during its movement towards the earth's surface.

The speciation and composition of a typical aqueous chloride rich fluid phase in equilibrium with a potassium rich quartzo-feldspathic rock at 500°C and 2 Kbar is determined to be somewhat acidic to neutral and contains a low concentration of Al. Such a fluid will promote heterogeneous nucleation of the product phases with a texture controlled by constant Al replacement. From an energy standpoint, there appears to be a coupling of surface reaction rates with transport and nucleation rates to minimize the entropy of these irreversible processes.

Intraplate magmatic intensity through time: a record of rate-controlled deep earth processes?

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A long-standing question of whether alkaline magmatism was scarce (or absent) in the early geologic record has received a new twist with the observation that carbonatite frequency has increased through Early Proterozoic to Recent. It has been argued that the data may be consistent with (a) increasing activity, or (b) steady-state eruption and destruction. If activity rate could be unambiguously discerned, it would offer an important constraint in consideration of Earth evolution. As the steady-state interpretation depends upon decreasing probability of preservation with age, the pattern may be sharpened by focussing on Africa, which has not suffered orogenic crustal descruction for much of the period under consideration. Since the late Precambrian, when the African plate became essentially anorogenic, the carbonatite/alkaline igneous time pattern emerges as spikes of activity, which correlate with external events. Until the Cretaceous the spikes are of similar amplitude, which may represent 'steady-state' eruption, but not destruction. In the Cretaceous and in Tertiary–Recent, however, unprecedented levels of activity were unleashed across the African plate. The Cretaceous 'storm' is also signalled in kimberlite activity peaks, especially in southern Africa. A lithospheric contribution to the magmatism is widely invoked, and a popular source rock for carbonatite/kimberlite/alkaline ultramafic activity is carbonated phlogopite peridotite. Such a protolith must be the product of sub- to near- solidus metasomatism of the mantle source. Levels of igneous activity must therefore partly reflect the extent of CO_2 and incompatible element sequestration in the continental lithosphere. Activity patterns need to be examined against this background, and in the light of global tectonics and stratigraphic geochemistry. This approach offers not only the prospect of better definition of long-term rates but also the possibility of identifying rate changes in the geologic record.